(8)

Abstract:

Source: JP9071405A2

PROBLEM TO BE SOLVED: To obtain high-purity hydrogen peroxide by irradiating hydrogen peroxide with light. SOLUTION: Hydrogen peroxide is irradiated with light to purify. Namely, since organic impurities in hydrogen peroxide are subjected to oxidative decomposition into a carbon dioxide gas and released to air by irradiating the hydrogen peroxide with light, the organic impurities in hydrogen peroxide can be removed. A method for efficiently irradiating a solution with light while stirring is preferable as a method for irradiating hydrogen peroxide with light. Although ozone occurs by irradiation with light, the ozone is naturally decomposed and it will cause no problems in the following treatments. The concentration of hydrogen peroxide is preferably 1-70wt.%. Removal of impurities in hydrogen peroxide, which has been conventionally impossible by purification through a distillation method or an ion exchange resin, can be carried out by irradiation with light more efficiently by purification by distillation method or an ion exchange resin after the irradiation.

Claims of JP9071405:

Machine_translation_Claims:

Claim 1 The purification method of the hydrogen peroxide characterized by irradiating light at a hydrogen peroxide.

Claim 2 The purification method of the hydrogen peroxide according to claim 1 characterized by distilling as after treatment.

Claim 3 The purification method of the hydrogen peroxide according to claim 1 characterized by making any one or more of ion exchange resin, adsorption resin, chelating resin, a reverse osmotic membrane, and the ultrafiltration membrane contact as after treatment.

Claim 4 The purification method of the hydrogen peroxide according to claim 1 characterized by contacting coincidence in ozone gas.

Claim 5 Claim 1 characterized by making a transition-metals compound coexist with a hydrogen peroxide as a catalyst, the purification method of the hydrogen peroxide of four publications.

Claim 6 The purification method of the hydrogen peroxide according to claim 5 which is at least one sort chosen from the group which a transition-metals compound becomes from iron, copper, the sulfate of chromium, a nitrate, a hydrochloride, a perchlorate, an oxide, and a hydroxide.

Claim 7 Claim 1 whose light to irradiate is ultraviolet rays, the purification method of the hydrogen peroxide of four publications.

Description of JP9071405:

Machine_translation Detailed Description of the Invention:

0001

Industrial Application This invention relates to the purification method of the hydrogen peroxide from which the impurity contained in hydrogen-peroxide liquid is removed. The hydrogen peroxide refined by the high grade using this invention is used especially suitable for washing of semi-conductor substrates, such as a silicon wafer.

0002

Description of the Prior Art Generally, a hydrogen peroxide performs removal of organic and an inorganic impurity with distillation, ion exchange resin, etc., and purification is performed. Generally organic impurities are removed by distillation or adsorption resin, and inorganic impurities (metal etc.) are removed by ion exchange resin. Moreover, the hydrogen peroxide of a high grade is further obtained by dipping in adsorption resin, ion exchange resin, etc. a hydrogen peroxide with the low impurity content obtained by distillation. Thus, the refined hydrogen peroxide of a high grade is widely used as a basic or acid hydrogen peroxide in washing of a silicon wafer etc., and whenever still higher purification is being required in connection with the densification of the latest integrated circuit.

0003

Problem(s) to be Solved by the Invention However, it is more difficult to manufacture the hydrogen peroxide of a high grade rather than a demand will be expected with the present purification technique from now on, for example, about organic impurities or colloidal silica, the removal is very difficult for it. Although it now is not still clear about the effect of when these impurities remain to a silicon wafer , the purification technique more than before which removes these impurities with high integration of a semi-conductor is demanded.

0004

Means for Solving the Problem As a result of inquiring wholeheartedly that the above-mentioned problem should be solved, this invention persons find out that it is very effective in a hydrogen peroxide to irradiate light, and came to complete this invention. That is, since oxidative degradation of the organic impurities in hydrogen-peroxide liquid is carried out, they serve as carbon dioxide gas and are emitted into air by irradiating light at a hydrogen peroxide, it becomes removable the organic impurities in a hydrogen peroxide . Although there is especially no limit in the approach of irradiating light at a hydrogen peroxide, the approach of stirring and irradiating light efficiently at liquid is desirable. Moreover, although ozone occurs by irradiating light, since it decomposes automatically, this ozone does not pose a problem by subsequent processing. Especially a limit may not be in the hydrogen peroxide which irradiates light here, and the hydrogen peroxide of the culmination of purification is sufficient, and a hydrogen peroxide with the high high impurity concentration made in manufacture is sufficient. Moreover, although there is especially no limit in the concentration of the hydrogen peroxide at this time, 1 - 70 % of the weight is preferably good.

0005 Moreover, the impurity in the hydrogen peroxide which was not able to be removed by purification by distillation or ion exchange resin becomes removable more efficiently by purification of subsequent distillation, ion exchange resin, etc. by carrying out an optical exposure conventionally. For example, first, by oxidation by optical exposure, the organic impurities which were not usually able to be removed by distillation are emitted into air as carbon dioxide gas, and decrease in number. Decomposition by this Tokimitsu exposure is inadequate, and the organic impurities which did not become to carbon dioxide gas exist in a hydrogen peroxide as low-molecular fatty acids, such as formic acid and an acetic acid. These low-molecular fatty acids become possible removing easily by purification by distillation or ion exchange resin after that . The metal of difficult colloid also becomes possible removal changing to an ion-like gestalt with usual ion exchange resin, such as colloidal silica, similarly, and removing by purification of ion exchange resin etc. after that by optical exposure, . Although what is necessary is just the purification method which especially a limit does not have about the purification after performing this optical exposure, and removes the impurity in a hydrogen peroxide, purification by distillation, ion exchange resin, chelating resin, adsorption resin, the reverse osmotic membrane, and ultrafiltration membrane is especially effective.

0006 These purification methods can obtain a high grade hydrogen peroxide by combining and using it. For example, the hydrogen peroxide which performed the optical exposure can be first refined by distillation, and dipping by the column method can be performed in the sequence of adsorption resin, an anion exchange resin, and cation exchange resin, or it can become, and the hydrogen peroxide of a high grade can be obtained. If it is this way of combining, and a method of obtaining the hydrogen peroxide of a high grade more about the number of combination, there will be especially no limit. Moreover, it is also effective to combine with these light exposure and to contact ozone. By contacting this ozone, the same operation as an optical exposure, i.e., oxidation of organic impurities, takes place, and more efficient purification is attained. Although there is especially no limit in a hydrogen peroxide about the approach of contacting ozone here, it is desirable to blow the ozone gas of high concentration and a high grade, and to perform stirring etc. Although there is especially no limit about stirring, efficient contact in the ozone gas by strong stirring is more desirable. Moreover, the method of using for dilution of hydrogen peroxide solution the high-concentration ozone water dissolved in ultrapure water etc. is also desirable. The ozone which dissolved into the hydrogen peroxide by these actuation does not pose a problem by subsequent processing, in order to decompose automatically.

0007 Moreover, the approach of adding a transition metal catalyst on the occasion of this optical exposure is also more desirable. As a transition metal catalyst, iron, copper, and chromium are desirable here. Moreover, about these metals, the thing of fusibility is desirable in water, such as a sulfate, a nitrate, a hydrochloride, a perchlorate, an oxide, and a hydrate. Although there is especially no limit also about the amount of the transition metal catalyst added here, since disassembly of a hydrogen peroxide promotes as a catalysis that it is too much abundant and removal by subsequent ion exchange resin becomes difficult, low concentration is desirable as much as possible. For example, as iron nitrate, 0.01-100 ppm is desirable still more desirable, and 0.1-10 ppm is desirable. As a light used by the approach of this invention, ultraviolet rays are effective. As the light source of ultraviolet rays, there are sunlight, a fluorescent lamp, a xenon lamp, a halogen lamp, a low-pressure mercury lamp high-pressure mercury lamp, etc., it is a xenon lamp, a halogen lamp, a low-pressure mercury lamp, and a high-pressure mercury lamp preferably, and they are a high-pressure mercury lamp and a low-pressure mercury lamp still more preferably. The example is shown below.

0008

Example

10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 1 organic impurities (TOC). It was 39 ppm when the organic high impurity concentration after processing was measured.

0009 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 2 organic impurities (TOC). When distillation purification of the obtained hydrogen peroxide was carried out, the organic impurities in a purification hydrogen peroxide were 29 ppm.

0010 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 3 organic impurities (TOC). It dipped in the column made from Teflon with a bore of 15mm , and a die length of 30cm filled up with Amberlite IR-120B(H mold, ORGANO CORP. make)20ml which is cation exchange resin about the obtained hydrogen peroxide space-velocity SV10hr-1. Subsequently, it dipped and refined space-velocity SV10hr-1 in the column made from Teflon with a bore of 15mm , and a die length of 30cm filled up with Amberlite IRA-400 (GCC acid type, ORGANO CORP. make) 20ml which is an anion exchange resin. The organic impurities in the obtained purification hydrogen peroxide were 26 ppm.

0011 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 4 organic impurities (TOC). At this time, the ozone gas of 200 mg/l was blown by 0.8 l/min. The organic impurities in the obtained hydrogen peroxide were 16 ppm.

0012 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 5 organic impurities (TOC). At this time, 1 ppm of iron nitrate were added as a metal catalyst. The organic impurities in the obtained hydrogen peroxide were 34 ppm.

0013 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 6 organic impurities (TOC). At this time, 1 ppm of copper chlorides were added as a metal catalyst. The organic impurities in the obtained hydrogen peroxide were 35 ppm.

0014 10min stirring was performed irradiating a high-pressure ultraviolet ray lamp (500W) at 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 7 organic impurities (TOC). At this time, 1 ppm of chromium sulfates were added as a metal catalyst. The organic impurities in the obtained hydrogen peroxide were 36 ppm.

0015 It is distillation purification ****** in 800ml of 31wt(s)% hydrogen peroxides which contain 50 ppm as example of comparison 1 organic impurities (TOC). The organic impurities in the obtained hydrogen peroxide were 44 ppm.

0016

Effect of the Invention According to this invention, an impurity can be removed at high effectiveness and adsorption resin, ion exchange resin, etc. can remove organic impurities

with low purification effectiveness efficiently especially. The hydrogen peroxide of the high grade obtained by this invention can be used suitable for washing of a silicon wafer.

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平9－71405

(43)公開日　平成９年(1997)３月18日

(51)Int.Cl.[6]	識別記号	庁内整理番号	ＦＩ		技術表示箇所
Ｃ０１Ｂ　15/013			Ｃ０１Ｂ　15/013		
Ｂ０１Ｊ　19/12			Ｂ０１Ｊ　19/12	Ｚ	
27/122			27/122	Ｍ	
39/04			39/04	Ｈ	
Ｃ０２Ｆ　1/32			Ｃ０２Ｆ　1/32		

審査請求　未請求　請求項の数７　ＯＬ　（全　３　頁）　最終頁に続く

(21)出願番号　特願平7－226676

(22)出願日　平成７年(1995)９月４日

(71)出願人　000004466
三菱瓦斯化学株式会社
東京都千代田区丸の内２丁目５番２号

(72)発明者　堺谷　ひさし
東京都葛飾区新宿６丁目１番１号　三菱瓦斯化学株式会社東京研究所内

(72)発明者　田中　一成
東京都葛飾区新宿６丁目１番１号　三菱瓦斯化学株式会社東京研究所内

(54)【発明の名称】　過酸化水素の精製法

(57)【要約】
【構成】過酸化水素を光を照射して精製を行う。
【効果】イオン交換樹脂等による精製では効率の低い不純物が除去され高純度に精製された過酸化水素を得ることができる。

【特許請求の範囲】
【請求項１】　過酸化水素に光を照射することを特徴とする過酸化水素の精製法。
【請求項２】　後処理として、蒸留をすることを特徴とする請求項１記載の過酸化水素の精製法。
【請求項３】　後処理として、イオン交換樹脂、吸着樹脂、キレート樹脂、逆浸透膜、限外沪過膜のいずれか一つ以上に接触させることを特徴とする請求項１記載の過酸化水素の精製法。
【請求項４】　同時にオゾンガスと接触させることを特徴とする請求項１記載の過酸化水素の精製法。
【請求項５】　触媒として、遷移金属化合物を過酸化水素と共存させることを特徴とする請求項１、４記載の過酸化水素の精製法。
【請求項６】　遷移金属化合物が鉄、銅、クロムの硫酸塩、硝酸塩、塩酸塩、過塩素酸塩、酸化物及び水酸化物からなる群から選ばれた少なくとも１種である請求項５記載の過酸化水素の精製法。
【請求項７】　照射する光が紫外線である請求項１、４記載の過酸化水素の精製法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は過酸化水素液中に含有する不純物を除去する過酸化水素の精製法に関する。本発明を用いて高純度に精製された過酸化水素は、特にシリコンウエハ等の半導体基板の洗浄に好適に用いられる。
【０００２】
【従来の技術】一般に過酸化水素は蒸留法やイオン交換樹脂等によって有機及び無機不純物の除去を行い精製が行われている。一般的には蒸留法または吸着樹脂等によって有機不純物が除去され、イオン交換樹脂によって無機不純物（金属等）が除去されている。また、蒸留法によって得られた不純物含量の低い過酸化水素を吸着樹脂やイオン交換樹脂等に通液することによって、更に高純度の過酸化水素が得られている。このようにして精製された高純度の過酸化水素はシリコンウエハ等の洗浄において塩基性もしくは酸性の過酸化水素として広く使用されており、最近の集積回路の高密度化に伴い、さらに高い精製度が要求されつつある。
【０００３】
【発明が解決しようとする問題点】しかし、現状の精製技術では今後要求が予想されるより高純度の過酸化水素を製造するのは難しく、例えば有機不純物やコロイダルシリカ等についてはその除去が極めて困難である。これらの不純物がシリコンウエハに残留した場合の影響については現在のところまだ明確ではないが、半導体の高集積化に伴いこれらの不純物を除去する従来以上の精製技術が要望されている。
【０００４】
【問題を解決するための手段】本発明者らは上記の問題を解決すべく鋭意検討した結果、過酸化水素に光を照射することが極めて有効であることを見いだし本発明を完成するに至った。即ち光を過酸化水素に照射することによって過酸化水素液中の有機不純物が酸化分解され炭酸ガスとなって空気中に放出されるため、過酸化水素中の有機不純物の除去が可能となる。過酸化水素に光を照射する方法に特に制限はないが、撹拌を行い効率的に液に光を照射する方法が好ましい。また、光を照射することでオゾンが発生するが、このオゾンは自然に分解してしまうのでその後の処理で問題とはならない。ここで光を照射する過酸化水素に特に制限はなく、精製の最終段階の過酸化水素でも良く、また製造で出来た不純物濃度の高い過酸化水素でも良い。また、この時の過酸化水素の濃度に特に制限はないが好ましくは１～７０重量％が良い。
【０００５】また、従来、蒸留法やイオン交換樹脂による精製で除去出来なかった過酸化水素中の不純物は、光照射することによって、その後の蒸留法やイオン交換樹脂等の精製でより効率的に除去が可能となる。例えば、通常蒸留法で除去出来なかった有機不純物は、まず光照射による酸化で炭酸ガスとして空気中に放出され減少する。この時光照射での分解が不十分で炭酸ガスへとならなかった有機不純物は蟻酸、酢酸等の低分子脂肪酸として過酸化水素中に存在する。これらの低分子脂肪酸はその後蒸留法やイオン交換樹脂による精製によって容易に除去することが可能となる。同様にコロイダルシリカなどの通常イオン交換樹脂で除去が困難なコロイド状の金属も光照射によってイオン状の形態に変化し、その後イオン交換樹脂等の精製で除去する事が可能となる。この光照射を行った後の精製に関しては特に制限はなく過酸化水素中の不純物を除去する精製法であれば良いが、特に蒸留法、イオン交換樹脂、キレート樹脂、吸着樹脂、逆浸透膜、限外沪過膜による精製が効果的である。
【０００６】これらの精製法は組み合わせて使用することによってより高純度な過酸化水素を得ることができる。例えば、光照射を行った過酸化水素をまず蒸留法で精製し、吸着樹脂、アニオン交換樹脂、カチオン交換樹脂の順序でカラム法による通液を行うとかなり高純度の過酸化水素を得る事が出来る。この組み合わせ方、組み合わせの数に関してはより高純度の過酸化水素を得る方法であれば特に制限はない。また、これら光照射に併せてオゾンを接触させることも有効である。このオゾンを接触させることによって光照射と同様な作用、即ち有機不純物の酸化が起こり、より効率的な精製が可能となる。ここで、過酸化水素にオゾンを接触させる方法に関しては特に制限はないが、高濃度、高純度のオゾンガスを吹き込み撹拌等を行うのが好ましい。撹拌に関しては特に制限はないが、強撹拌によるオゾンガスとの効率的接触がより好ましい。また、超純水等に溶解させた高濃度のオゾン水を過酸化水素水の希釈に用いる方法も好ま

しい。これらの操作で過酸化水素中に溶解したオゾンは自然に分解してしまうため、その後の処理で問題とはならない。

【０００７】また、この光照射に際し、遷移金属触媒を添加する方法もより好ましい。ここで遷移金属触媒としては鉄、銅、クロムが好ましい。また、これらの金属に関しては硫酸塩、硝酸塩、塩酸塩、過塩素酸塩、酸化物、水和物等の水に可溶性のものが好ましい。ここで添加する遷移金属触媒の量に関しても特に制限はないが、あまりに多量であると触媒作用として過酸化水素の分解が促進してしまい、またその後のイオン交換樹脂による除去が困難となるため可能な限り低濃度が好ましい。例えば、硝酸鉄としては０．０１～１００ｐｐｍが好ましく、更に好ましくは０．１～１０ｐｐｍが好ましい。本発明の方法で用いられる光としては、紫外線が効果的である。紫外線の光源としては、太陽光、蛍光灯、キセノンランプ、ハロゲンランプ、低圧水銀ランプ高圧水銀ランプ等があり、好ましくはキセノンランプ、ハロゲンランプ、低圧水銀ランプ、高圧水銀ランプであり、更に好ましくは高圧水銀ランプ、低圧水銀ランプである。以下にその実施例を示す。

【０００８】

【実施例】

実施例１

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。処理後の有機不純物濃度を測定したところ３９ｐｐｍであった。

【０００９】実施例２

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。得られた過酸化水素を蒸留精製したところ、精製過酸化水素中の有機不純物は２９ｐｐｍであった。

【００１０】実施例３

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。得られた過酸化水素をカチオン交換樹脂であるアンバーライトＩＲ－１２０Ｂ（Ｈ型、オルガノ（株）製）２０ｍｌを充填した内径１５ｍｍ、長さ３０ｃｍのテフロン製カラムに空間速度ＳＶ１０ｈｒ$^{-1}$に通液した。次いで、アニオン交換樹脂であるアンバーライトＩＲＡ－４００（重炭酸型、オルガノ（株）製）２０ｍｌを充填した内径１５ｍｍ、長さ３０ｃｍのテフロン製カラムに空間速度ＳＶ１０ｈｒ$^{-1}$に通液し、精製した。得られた精製過酸化水素中の有機不純物は、２６ｐｐｍであった。

【００１１】実施例４

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。この時、２００ｍｇ／ｌのオゾンガスを０．８ｌ／ｍｉｎで吹き込んだ。得られた過酸化水素中の有機不純物は１６ｐｐｍであった。

【００１２】実施例５

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。この時、金属触媒として硝酸鉄１ｐｐｍを添加した。得られた過酸化水素中の有機不純物は３４ｐｐｍであった。

【００１３】実施例６

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。この時、金属触媒として塩化銅１ｐｐｍを添加した。得られた過酸化水素中の有機不純物は３５ｐｐｍであった。

【００１４】実施例７

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに高圧紫外線ランプ（５００Ｗ）を照射しながら１０ｍｉｎ撹拌を行った。この時、金属触媒として硫酸クロム１ｐｐｍを添加した。得られた過酸化水素中の有機不純物は３６ｐｐｍであった。

【００１５】比較例１

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１ｗｔ％の過酸化水素８００ｍｌを蒸留精製行った。得られた過酸化水素中の有機不純物は４４ｐｐｍであった。

【００１６】

【発明の効果】本発明によれば、不純物を高い効率で除去することができ、特に吸着樹脂、イオン交換樹脂等で精製効率の低い有機不純物を効率よく除去することができる。本発明により得られた高純度の過酸化水素はシリコンウエハの洗浄に好適に使用し得るものである。

フロントページの続き

(51)Int.Cl.^{6}	識別記号	庁内整理番号	ＦＩ	技術表示箇所
// Ｈ０１Ｌ　21/304	３４１		Ｈ０１Ｌ　21/304	３４１Ｌ